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BY

L. L. HIRST, L. C. SKINNER, AND E. E. DONATH

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IMPROVEMENTS IN HYDROGENATION OF COAL[1/]

By L. L. Hirst,[2/] L. C. Skinner,[3/] and E. E. Donath[4/]

INTRODUCTION

Two processes are available for the production of synthetic fuels from coal - high-pressure hydrogenation and the carbon monoxide-hydrogen synthesis. This paper presents some ideas and new developments in coal hydrogenation that have been incorporated in an estimate for the production of 30,000 barrels per day of liquid fuels, mainly gasoline. A few comparisons of the processes will be helpful before discussion of the details of proposed improvements in the hydrogenation process.

The principle of the high-pressure hydrogenation process is the addition of hydrogen at pressures in the range of 3,000 to 10,000 p.s.i. to coal at elevated temperature and with the help of catalysts. On the other hand, the principle in the Fischer-Tropsch synthesis is the complete break-down of coal into a mixture of carbon monoxide and hydrogen, followed by the catalytic combination of these two gases into hydrocarbons on suitable catalysts. For the synthesis, moderately elevated pressures of about 350 p.s.i. will be used in the immediate future, although it can be carried on at atmospheric pressure with certain catalysts.

The products of these two processes using coal as raw material are almost as different as hydrocarbons can be. The products of the high-pressure hydrogenation of coal reflect the original constitution of the coal. They are, therefore, rich in ring compounds, both aromatic and naphthenic, but, due to the action of highly compressed hydrogen and catalyst, are saturated and very stable. These constituents give the gasoline a high octane number and excellent rich-mixture performance, combined with good gum and storage stability. Therefore, this gasoline is suitable for aviation gasoline or base stock. The Diesel fuel can be hydrogenated to a centane number of 45 or higher, which is entirely satisfactory for operating normal Diesel

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engines. Both Diesel and jet fuels made by coal hydrogenation have very low pour and freezing points and high heating value per unit of volume. Coal hydrogenation is also suitable for the production of fuel oil. By-products from coal hydrogenation include phenols and aromatics, such as benzene, toluene, xylenes, and solvents, as well as polynuclear aromatics. The off-gases formed during the hydrogenation process are mainly saturated and have a high content of isocompounds, such as isobutane and isopentane.

On the other hand, products from the carbon monoxide-hydrogen synthesis are mainly paraffins and olefins and have a negligible content of ring compounds. Similarly, the oxygen-containing byproducts are aliphatic alcohols, aldehydes, ketones, and acids. The off-gases are rich in olefins and have only a small content of isocompounds.

From this it may be seen that, as far as the quality of products is concerned, these two processes are complementary. Both types of products are needed. In several phases of these processes, such as gas production, power generation, off-gas utilization, etc., a combination would be useful. Commercial-size plants are required to obtain final results on the economy of both processes and the quality of the products.

The economy of both processes depends largely on future chemical and engineering developments, especially in a field common to both, namely, gas production. From the cost standpoint, coal consumption and the capital costs are the main factors. The total consumption of coal for both processes is similar. At present, the coal consumption of the high-pressure hydrogenation process seems, however, to be somewhat lower for the majority of the coals available in this country, especially in the Rocky Mountain area, because high-volatile coals, subbituminous coals, and lignites are especially suited to the hydrogenation process. The throughput and space-time yields of oil are higher for younger coals - those high in volatile matter and low in carbon content. These younger coals also form less asphalts and gases during the primary hydrogenation step; therefore, the oil recovery is easier and the hydrogen consumption lower. Further characteristics of good hydrogenation coals are low ash and high net hydrogen content. A low ash content decreases the oil losses with the hydrogenation residue. High-net-hydrogen coals need less hydrogen in the process and usually are easier to hydrogenate.

GENERAL DESCRIPTION OF HYDROGENATION PROCESS

The high-pressure hydrogenation of coal, as figure 1 shows, is normally performed in two stages. The first is the conversion of coal made to a paste in the so-called liquid phase with a finely divided catalyst to a middle oil. This middle oil then is converted over a solid catalyst in vapor phase to gasoline, jet, or Diesel fuel. Products of the liquid phase can be used as fuel oil; due to their content of phenols and nitrogen compounds, however, a finishing by vapor-phase hydrogenation is necessary if gasoline, jet fuel, or Diesel fuel is produced. The vapor-phase catalyst performs conversion of this middle oil to a stable, sulfur-free final product of the desired boiling range and hydrogen content. For liquid-phase hydrogenation the coal is deashed, if necessary, and is ground and made to a paste with catalyst

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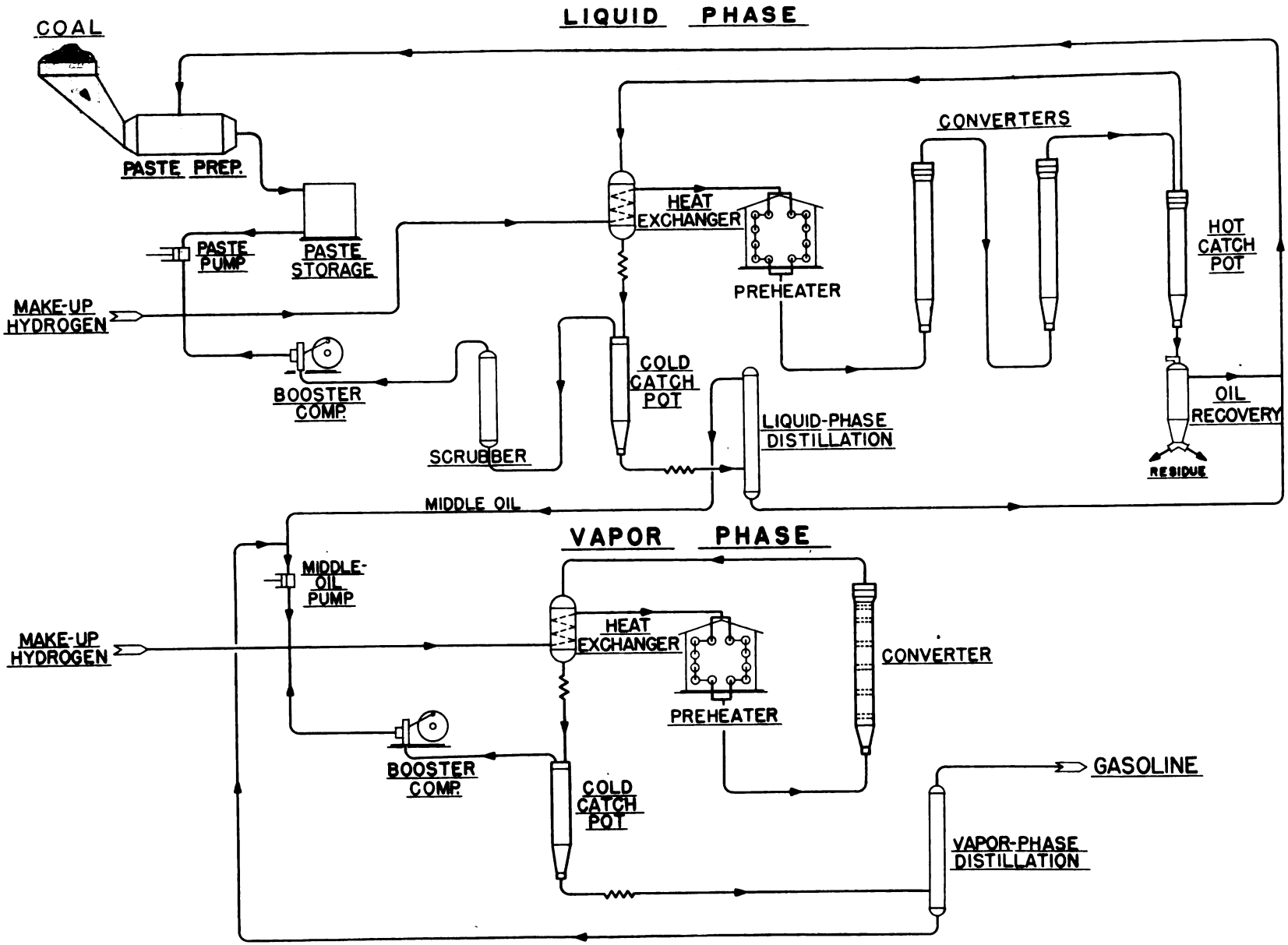

Figure 1. - Coal hydrogenation.

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and recycled heavy oil. The paste, containing about 50 percent coal, is brought to 10,000 p.s.i. pressure with feed pumps and joins the hydrogen stream, consisting of make-up and recycled hydrogen.

The mixture of hydrogen and paste is preheated by heat exchange and gas-fired preheaters nearly to reaction temperature, then enters several converters in series. In the first converter, because of the heat of reaction, the temperature rises to a reaction temperature of about 900° F. and is held down to that level by the admission of cold recycle gas.

The reaction products, having passed the converters, enter the so-called "hot catchpot". The heaviest oil fractions and asphalt, together with ash, catalyst, and about 1 to 4 percent of unconverted coal, are withdrawn at the bottom and discharged by means of special let-down valves. This slurry, the so-called "H.O.L.D." goes to the oil-recovery plant. The recovered oil is recycled to the coal-pasting plant. The hydrogen and oil vapors from the hot catchpot are used to preheat the feed in heat exchangers and then cooled and separated from the hydrogen in the cold catchpot. The hydrogen goes to an oil scrubber to remove inerts and gaseous hydrocarbons formed in the process and is then returned to the start of the process by booster compressors. The condensed oil is let down from the cold catchpot and distilled into an overhead middle-oil fraction with about 620° end point, and bottoms. The bottoms are used as pasting oil. The liquid-phase middle oil contains about 15 percent tar acids. They can be recovered and are, as will be seen later, a very valuable byproduct. About 8 percent by weight of the finished gasoline is phenol, cresols, and xylenols.

The middle oil is injected to the vapor phase. The flow in the vapor-phase unit is similar to that from the liquid phase, but this phase contains no hot catchpot. The main difference is that the converters are filled with solid lump catalyst, and the oil passing over the catalyst is evaporated in the hydrogen stream. The products of the vapor phase are distilled in a conventional way into gasoline and unconverted middle oil. The middle oil is recycled into the vapor phase and converted to gasoline. Using different catalysts, the vapor-phase product can also be utilized as Diesel or jet fuel. After a caustic wash to remove hydrogen sulfide, the gasoline is a low-sulfur and stable product and does not require further treatment. The vapor-phase hydrogenation is a very efficient and, by using different catalysts, a versatile process. The only byproducts formed are gaseous hydrocarbons, their quantity depending on the final product, being 2 to 15 percent by weight of the converted feed.

The following table shows some data of bituminous-coal hydrogenation products obtained in experimental units. The boiling range can easily be adjusted if specifications make that necessary.

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	Motor gasoline	Aviation gasoline	Jet fuel	Diesel fuel
°A.P.I.	51	54	35	32
Boiling range ..... °F.	95 - 350	105 - 320	320 - 570	350 - 600
Aromatics ..... percent	45	43	-	-
Naphthenes ..... do.	35	35	-	-
Paraffins ..... do.	18	20	-	-
Olefins ..... do.	2	2	Below 3	Below 3
Sulfur	Below 0.05	Below 0.02	Below 0.1	Below 0.1
Octane No. M.M.	78	80	-	-
Octane No. M.M. + 3 m.l. TEL per gal.	90	94	-	-
Cetane No.	-	-	-	45
Reid vapor pressure .. p.s.i.	10	7	Below 2	Below 2
Freezing point ..... °F.	Below - 76	Below - 76	Below - 76	Below - 40

Due to their high degree of saturation, all these products meet the normal gum specifications. In comparison to the data given for the hydro-gasoline, it may be mentioned that carbon monoxide-hydrogen synthesis gasoline obtained with an iron catalyst has about the same clear octane number but contains 60 percent olefins and only a negligible amount of aromatics and naphthenes.

Instead of coal, heavy residues, shale oil, gas oil, etc., can also be hydrogenated. The throughput is higher and the hydrogen consumption lower than for the hydrogenation of coal.

The hydrogenation of coal will be tested in the Louisiana Demonstration Plant with a rated capacity of about 200 barrels of gasoline per day.

PROGRESS IN THE HYDROGENATION PROCESS, 30,000 BBL. PER DAY ESTIMATE

The manufacturing costs of hydrogenation gasoline are determined by the coal consumption, the required labor, and the capital costs. The Bureau of Mines was directed by Public Law 290, 78th Congress, to furnish cost data on synthetic-fuel processes. Preliminary studies showed that a plant for the production of about 30,000 bbl. per day of gasoline and liquefied petroleum gas will consist of large units to permit low labor costs and will contain several of these units in the different stages so that a steady operation can be maintained. This plant consists of the following sections:

1. Hydrogen production and compression.
2. Hydrogenation proper.
3. Product distillation.
4. Power and utilities production and distribution.

For the production of hydrogen in the 30,000-barrel-per-day plant, coal gasification with oxygen and the methane-steam process for converting excess off-gases are provided. Hydrogen production, with compression as the largest power consumer, determines to a great extent the power requirements and the thermal efficiency of the process. It may be mentioned that the power plant, including the process and heating-steam production, has about 40 percent thermal efficiency, the lowest of all the plant sections. It is therefore

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important to note that new processes for gasification under a pressure of about 300 p.s.i. are being developed which cut the compression costs and increase the thermal efficiency. These pressure gasification processes are are still in the experimental stage; but they are needed for the hydrogenation process as well as the carbon monoxide-hydrogen synthesis, and their development to commercial operation is only a question of time.

The design of the hydrogenation proper also must be aimed toward a reduction in plant costs and increase in thermal efficiency. By using large converters of 700-cu. ft. volume - twice the size of the converters used commercially in Europe - not only the construction, but also the operating costs were decreased. A further increase in capacity per unit and in yield will be possible owing to complete automatic control of the hydrogenation stalls. The latest European experience in this field showed very significant improvements due to smoother operation of automatically controlled stalls. A decrease in equipment costs was also achieved by using wrapped, high-pressure vessels. These vessels were developed in Germany beginning about 10 years ago and are cheaper and stronger than forged vessels. They consist of interlocked ribbons wound hot, with the proper stress, around a core tube. Further improvements in the high-pressure section were achieved by careful selection of construction materials, an elaborate heat exchange and utilization of the heat of reaction to preheat the feed in a preheat converter, simpler steam-driven paste pumps, and cheaper construction of the cooler.

For distillation of products and recovery of liquefied petroleum gas, modern refinery practice was followed. An important part of the hydrogenation process is also separation of heavy oil from the hydrogenation residue. Instead of the centrifuges and flash distillation hitherto used, the delayed coking process was chosen, which promises high yields of oil at low costs.

The newest process development for a single-stage operation at 10,000 p.s.i. was selected for the vapor-phase part of the plant. The catalyst for this operation is cheap and has long life - German commercial experience showed at least 1 year. As shown above, the gasoline made with this catalyst is high in aromatics and octane number. Experiments have indicated that further improvements in octane number are possible. The conversion of middle oil to gasoline per pass is 50 percent. Complete middle-oil conversion is obtained by recycling the unconverted middle oil. The yield of finished gasoline is 100 percent by volume.

The plant for hydrogenation of a low-ash, high-volatile bituminous coal is designed to produce the following products:

	Bbl. per day
Gasoline	22,100
Liquefied petroleum gas	7,250
Phenol, cresols, and xylenols[1]	1,330
Total	30,680

[1] 467,000 lb. per day.

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Corresponding to 2.5 barrels of product per ton of coal, the coal consumption is 12,500 tons per day. The following capital costs for this plant were obtained:

Capital cost for hydrogenation plant to operate on low-ash, high-volatile, bituminous coal

	Million dollars
Hydrogen production and compression..	61
Hydrogenation, including coal preparation	80
Distillation, tankage, and phenols recovery	16
Power, utilities, and general plant facilities	87
Total	244

For the gasoline, the following manufacturing costs were estimated:

	Cents per gallon of gasoline
Coal at $3.56 per ton	4.8
Labor ($1.75 per hr.) and supervision	1.3
Maintenance	2.1
Overhead, supplies, indirect costs	3.2
Amortization, 15 years	4.8
Taxes (1 percent)	.7
Subtotal	16.9
Credits	
L.P.G.1/ at 8¢ per gal.	2.6
Phenols at 10¢ per lb.	5.0
Total net costs	9.3
Credit for L.P.G. only, phenols converted to gasoline	13.3

1/ Liquefied petroleum gas.

To this figure, return on investment, sales expenses, etc., must be added to obtain the sales price.

If this plant were built without the improvements, such as pressure gasification, fully automatic control, wrapped vessels, etc., the plant costs would be about 25 percent higher and the gasoline-manufacturing costs would be about 4 cents per gallon greater.

The thermal efficiency of the plant described is 48 percent, based upon the heating value of the total coal used and of the gasoline, liquefied petroleum gas, and phenols obtained as products. This high thermal efficiency,

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in comparison to 33 percent obtained in German coal-hydrogenation plants, is a result of the improvements mentioned and the fact that the high-volatile, low-ash coals abundantly available in this country are especially suitable for the hydrogenation process.

It seems obvious that the coal-hydrogenation process will be an important part of the future synthetic fuels industry. Its coal consumption and costs basically are not higher than those of a carbon monoxide-hydrogen synthesis plant using coal. The chemical nature of the coal hydro-products and their content of aromatics are valuable, not only in their utilization as fuels, but also in the field of chemicals. The hydrogenation process can also be used for complete conversion of heavy residues and shale oil to gasoline and other fuels. In Europe it was found on commercial scale that service factors of 90 percent and better were achieved. The safety of the high-pressure process as reflected in the accident rate was better than in atmospheric pressure gasification or distillation plants. Because better construction materials are now available in this country, a further improved performance can be expected.

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